Magnetic Properties of Fe₃O₄ Films Grown by Epitaxial Electrodeposition on the Low Index Planes of Gold

J.A. Switzer¹, T.A. Sorenson¹, S.A. Morton², and G.D. Waddill²

¹Department of Chemistry and Graduate Center for Materials Research

²Department of Physics and Graduate Center for Materials Research

University of Missouri-Rolla, Rolla, Missouri 65409-1170, USA

Spin-dependent charge transport is currently receiving a lot of attention due to potential applications in giant magnetoresistive (GMR) devices such as magnetic field sensors, magnetoresistive random access memories (MRAM), read heads, and galvanic isolators. 1,2 These devices require a source of spin-polarized electrons. Magnetite, Fe₃O₄, is a promising source of spin-polarized carriers, because density-functional theory spin-resolved density of states calculations have suggested that electrons at the Fermi level are -100% spin polarized. 3,4 Magnetite is a mixed-valence 3d transition metal oxide that has an inverse spinel structure (space group Fd3m) with a lattice constant of 0.8397 nm. The tetrahedral sites of the spinel structure are entirely occupied by Fe³⁺, whereas the octahedral sites are occupied half by Fe²⁺ and half by Fe³⁺. Fe₃O₄ undergoes a metal-to-insulator Verwey transition at 120 K and the Curie temperature of magnetite is 860 K. Recently, GMR effects greater than 500% have been reported at room temperature for Fe₃O₄ nanocontacts. 5

We have electrodeposited galvanostatically epitaxial Fe₃O₄ films on Au(111), a system with a 3% lattice mismatch. These films are $\sim 0.5 \, \mu m$ thick and have a (111) orientation. X-ray diffraction and SEM results establish that the magnetite films consist of twinned domains rotated by 180° with respect to each other. For the spin-polarized photoemission measurements a magnetic field from an *in situ* electromagnet is applied to the sample either in the plane of the sample or perpendicular to that plane. The field is then removed and the photoemission measurements are performed in remanence. The spin-resolved measurements were done at Beamline 7.0.1 with the spin-resolved endstation. The energy of the excitation beam was ~ 160 eV. Emitted photoelectrons were collected and filtered by a PHI 10-360 SCA hemispherical electron energy analyzer and then passed into a micro-Mott detector to resolve the electron spins. The total energy resolution for the spin resolved measurements was ~ 0.5 eV. Finally we have measured Fe L edge and O K edge XAS as well as Fe MXCD for these samples at Beamline 4.0. For the MXCD measurements, the sample was magnetized in situ and the measurements were made in remanance. All measurements were made at room temperature. Prior to the photoemission, XAS, and MXCD measurements the samples are briefly sputtered and then annealed in an oxygen environment. This produces LEED patterns consistent with the presence of rotationally twinned Fe₃O₄(111), but the films are rather poorly ordered. Photoemission always observes a trace amount of surface carbon.

The Fe L edge MXCD. These results are virtually indistinguishable from results reported by Kim *et al.* for a bulk magnetite sample. Figs. 4 and 5 show the spin-resolved photoemission results for these samples. The polarization at the Fermi level is approximately – 40% with a change in the sign of the polarization observed at ~1 eV binding energy. The reasons for the observed deviation from the predicted value of –100% is not known. There are two recent repots for *in situ* prepared Fe₃O₄ films that report either – 50% or – 80% ¹⁰ spin-polarization. The first result

is attributed to correlation effects that set an upper limit on the spin-polarization of $-67\%^{11}$ while the latter is regarded as evidence for half-metallic behavior. The discrepancy between these various results requires further investigation.

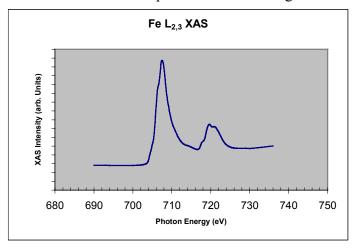


Figure 1. Fe L edge x-ray absorption for thick magnetite film on Au(111).

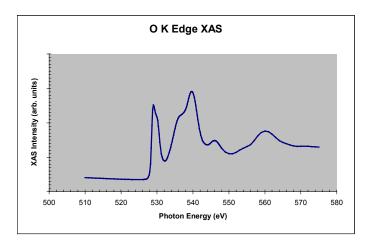


Figure 2. O K edge x-ray absorption for thick magnetite film on Au(111).

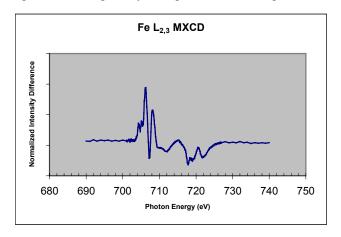


Figure 3. Fe L edge magnetic x-ray circular dichroism for thick magnetite film on Au(111).

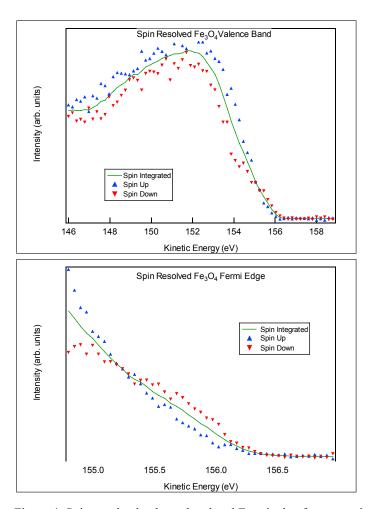


Figure 4. Spin-resolved valence band and Fermi edge for magnetite on Au(111).

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The National Science Foundation (CHE 9816484, DMR 0071365, and DMR 0076338) and the Foundation for Chemical Research are gratefully acknowledged for financial support of this work.

Principal investigator: Dan Waddill, Department of Physics and Graduate Center for Materials Research, University of Missouri-Rolla. Telephone: 573-341-4797. Email: waddill@umr.edu.